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No. V.

Experiments on the Production of Air by the Freezing of Water. By Dr. JOSEPH PRIESTLEY.

Read April 18, 1800. **I**N 1793, when I was in England, I published a course of experiments on *the generation of air from water*, and after my arrival in this country, I resumed the experiments, and published a *sequel* to them. The result of the whole was that, after all air had been extracted from any quantity of water, either by heating, or by taking off the pressure of the atmosphere, when ever any portion of it was converted into vapour, a bubble of permanent air was formed, and this was always phlogificated. The process with the Torricellian vacuum I continued some years, and found the production of air equable to the last. The necessary inference from this experiment is, either that water is convertible into phlogificated air, or that it contains more of this air intimately combined with it than can be extracted by these processes in any reasonable time.

Finding that no air is contained in *ice* that is free from visible bubbles, I thought to ascertain the truth of one or other of these hypotheses by exposing to frost a quantity of water from which I had, by repeated processes with the Torricellian vacuum, expelled all the air that I possibly could; thinking, that if it really contained no air, it would appear by the ice being perfectly solid; so that when it was melted no air would be got from it. This experiment I repeated several times, but always found that though the outside of this ice was perfectly transparent, and free from air, the central parts were opaque; and though there were no distinct air bubbles in it, yet when it was melted a great number of bubbles issued from it. The whole quantity, however, was not greater

greater than might have been produced from the same water in the other processes in a reasonable time; and in them the production of air had no limit.

Disappointed in my expectations of getting by this means ice perfectly free from air, (which when a large quantity of water freezes very slowly it is easy to do, the air contained in it retiring from that which is frozen to that which remains fluid) I dissolved ice that was perfectly transparent, and therefore free from air, in vessels containing mercury, and exposed it to frost a second time. But I always found that when the whole of it was frozen, though the extreme parts were transparent, and therefore free from air, the central parts were opaque, and when dissolved yielded air. And though I repeated this process ten or a dozen times with the same water, always letting out the air that was procured by freezing presently after it was extricated under mercury, and before it could have been reabsorbed, yet on exposing it to another freezing, I never failed to get more air; and the harder the frost was the more air I procured.

As there is an evaporation from ice, no less than from water, the interstices formed by the crystallization of the water when it is converted into ice will soon be filled with *vapour*; and this vapour, like that which is formed by heat, becomes, I suppose, the basis of a quantity of air. Since, however, ice that is the most transparent swims in water, this also must have interstices; but they contain no air; being such as exist in the most solid bodies, in which (gold itself not excepted) the component particles are not in perfect contact; since they are reduced into less dimensions by cold.

As the vessels I made use of in these experiments were either cylindrical jars, or conical wine glasses, and consequently the bubbles of air procured by freezing were exposed to a considerable surface of water, and would in
time

time (though not, I found, in the course of a day) have been absorbed by the water, now free from air, I procured glass vessels of a conical form, terminating in narrow tubes, into which the air dislodged from the ice might ascend, and not be subject to be absorbed. I was so fortunate as to have several of such vessels, and they completely answered my purpose for five or six processes. These vessels were first filled with mercury, and then I introduced into them a quantity of water freed from air by previous freezing; and when, after exposure to frost, the ice was melted, the air dislodged from the ice ascended into the narrow tubes, and remained without any sensible diminution of bulk several days; and every time that the water was exposed to the frost, an addition was made to it. At length, however, though the vessels were very strong, and contained much mercury, which by its tendency to descend would give the water room to expand with the less danger of breaking the vessel, none of them served for more than the number of processes above-mentioned.

After the breaking of my glass vessels, I got other cylindrical ones made of *iron*, seven or eight inches in height, and near three inches wide at the bottom, the upper orifice closed with a cork and cement, in the centre of which was a glass tube, the diameter of which was about a fifth of an inch. And as the glass tube was in the greatest danger of breaking by the freezing of the water, and this had happened several times before, notwithstanding all my care to guard it from the frost, I now made use of snow and salt, to freeze the water in the iron vessel only, placed in a vessel of mercury, having been previously filled as the glass vessels had been.

The water on which I now operated was about three ounces, and it had been made as free as possible from air by previous freezing. With this apparatus I repeated the

the process of freezing nine times, without changing the water, and the last portion of air that I procured in this manner was as great as any of the preceding; so that there remained no reasonable doubt, but that air might be produced from the same water in this manner *ad libitum*. Having got near two inches of air in the glass tube, I put an end to the experiment; and examining the air, found it to be wholly *phlogisticated*, not being affected by nitrous air, and having nothing inflammable in it.

During the process of freezing the air in the tube was generally compressed into about one-fifth of its usual bulk; but, when I began to thaw the ice, which I did by means of hot water in the place of the freezing mixture, it soon expanded to its former dimensions, and no sensible portion of it was absorbed during the whole process, which was about a week. Sometimes the violence of the pressure, occasioned by the expansion of the water in freezing, would force a little water out of the vessel between the cork and the glass tube, or the iron vessel, which presently became ice. This I always carefully removed, and applied fresh cement to the place, to prevent the introduction of any air from without before I began to melt the ice. And that no external air had entered, was evident both from the manner in which the air was produced as the water recovered its fluidity, and from the quality of it when examined after the process.

In the course of the experiments with the glass vessels a phenomenon occurred that was wholly unexpected by me, and which was very amusing. Having left the vessels filled partly with water and partly with mercury in the evening, I generally found them in the morning seemingly quite full of mercury, every part of the ice within the vessel being covered with it. This must have been occasioned by a vacuum having been formed between the glass and the ice, and into this the mercury had

had been drawn up on the principle of the capillary tube. When this was not the case, the interstices of the ice towards the centre were filled with thin laminæ of mercury, which also exhibited a curious appearance.

Sometimes, when there was no mercury between the glass and the ice, an interstice was made between them when they were placed within the influence of the fire. In these circumstances I have seen the mercury drawn up to the height of several inches. As this space was enlarged by the increase of the heat, the laminæ of mercury were contracted, till coming into the form of balls, too heavy to be supported, they fell down to the mass of mercury in the basin.

The most natural inference from these experiments is that *water*, when reduced by any means to the state of *vapour*, is in part converted into phlogisticated air; and that this is one of the methods provided by nature for keeping up the equilibrium of this constituent part of the atmosphere; as the influence of *light on growing vegetables* is the means of recruiting that other part of it; and both of them are subject to absorption and diminution in several natural processes. Inflammable air I have also shewn to be convertible into phlogisticated air; and this is another means of supplying the atmosphere with this ingredient in its composition.

That water contains phlogiston I have shewn to be probable from several considerations, especially that of its resembling metals in their property of being conductors of electricity, for these substances certainly contain phlogiston, if there be any such thing. Mercury also becomes super-phlogisticated by agitation in water, and this without limit, and without changing either the water or the mercury; and the remaining water contains no more oxygen than before, for the air expelled from
it

it is not more pure but considerably less so, and it is perfectly free from acidity.

I would farther observe that these experiments, which prove the conversion of water into phlogisticated air, are inconsistent with the antiphlogistic theory, which makes water resolvable into dephlogisticated and inflammable air; but that they are highly favourable to the hypothesis of water being the basis of every kind of air, the difference between them depending upon the addition of some principles which we are not able to ascertain by weight. Also, if any species of air be entitled to the appellation of *hydrogen*, it is phlogiston, and not inflammable air.